Electronic Supplementary Information

Solar-to-hydrogen Efficiency Exceeding 2.5% Achieved for Overall Water Splitting with All Earth-abundant Dual-photoelectrode

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Experimental

1. Materials

All chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water (resistivity > 18 MΩ cm). The FTO (fluorine-doped tin oxide, < 14 Ω/square) conductive glass was purchased from Nippon Sheet Glass Company (Japan) and was ultrasonic cleaned with acetone, ethanol and deionized water for 20 min each prior to use.

2. Fabrication of FeOOH/Mo:$BiVO_4$ Fe_2O_3, WO_3 and CoPi electrodes

Mo:$BiVO_4$ electrodes were prepared by electrodeposition as previously reported[1, 2] except that 10.6 mg $MoCl_3$ (99.5%, Alfa Aesar) was added into the deposition solution. Mo:$BiVO_4$ electrodes were loaded with FeOOH cocatalyst via PEC oxidation of $FeCl_2.xH_2O$ (99%, Alfa Aesar).[1] The photodeposition was carried out in a three-electrode cell. A 140 W Xe lamp with light intensity filtered to about 2 mW cm^{-2} through a neutral density filter was used as light source. The current pulses alternated between 10 μA cm^{-2} for 3 s and 1 μA cm^{-2} for 2 s. The optimized deposition time of FeOOH was about 3 h when the potential passed through a minimum and began to increase. FeOOH/$BiVO_4$-pourous electrodes were prepared as recently reported.[3]

Fe_2O_3-FTO electrodes were fabricated by chemical bath deposition and annealing method. Typically, 5 mmol $FeCl_3$ $6H_2O$ (97%~100.2%, Alfa Aesar) and 0.3 g urea were dissolved in 50 mL water. Then FTO (2 cm×2 cm) was placed in the vessel and maintained at 100 ^{o}C for 4 h. The resulting pale yellow electrode was rinsed with water and dried at 80 ^{o}C for 1 h. Finally, the film was annealed in air at 500 ^{o}C for 3 h and 750 ^{o}C for 10 min to get the desired bright red α-Fe_2O_3 electrode.

WO_3-FTO electrodes were fabricated by d.c. reactive magnetron sputtering system (Kurt J. Lesker Company PVD75) with a W target (> 99.95%). The distance between the target and the sample was 15 cm. After pumping down to 7×10^{-7} torr, O_2 and Ar gases were introduced into the chamber. The oxygen partial pressure and the total sputtering pressure were 2 mtorr and 7.5 mtorr, respectively. The rotation speed of the substrate was 20 rpm. The sputtering power of W target was about 150 W and the sputtering time was 1 h. Finally, the as-prepared electrodes were calcined at 500 ^{o}C for 2 h.

CoPi-FTO electrodes were prepared by electrodeposition at 1.07 V vs. SCE from a 0.1 M sodium phosphate (pH 7) containing 0.5 mM $Co(NO_3)_2$ (≥ 99%, Sinopharm Chemical) with an optimized deposition time when the current passed through a maximum and began to decrease.

3. Fabrication of Ni/Si-cell photocathodes

Si-cells used for photocathode fabraication are commercial Si-cells (Hanergy, China). Two types of Si-cell with different V_{oc} and J_{sc} (Fig. S1): one is triple-junction Si_A composed of one layer of amorphous Si and two layers of nanocrystal Si and the other is double-junction Si_B, were used. The anode side of the Si-cell was connected with the photoanode using Cu wire and Ag conductive adhesive. The cathode side of the cell is deposited with Ni cocatalyst (about 100 nm in thickness) by magnetron sputtering. The cell was illuminated from the FTO side.

4. Fabrication of Pt/p-Si nanowire array (NW) and Pt/TiO_2/Ti/p-Si photocathodes

The Pt/p-Si NW photocathode was prapared from a p-Si wafer by the MCEE method.[4] Backside ohmic contact is formed by depositing 200 nm Al layer via vacuum vapor deposition. Pt/TiO_2/Ti/p-Si photocathodes were prepared by d.c. reactive magnetron sputtering according to the previously reported method.[5] The backside of the Pt/TiO_2/Ti/p-Si electrode was also deposited with 200 nm Al layer, and then the electrode were post treated in Ar atomsphere under 400 ^{o}C for 90 min. Before PEC measurement, the backside of p-Si electrode was first connected to a Cu wire using Ag conductive adhesive and then is fully sealed with epoxy resin and the frontside is painted with epoxy resin in order to fix the electrode area.

5. Characterizations and photoelectrochemical measurements

Samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer using Cu Kα radiation (operating voltage: 40 kV, operating current: 200 mA, scanning rate: 5 ° min^{-1}). Electrode morphologies were examined by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (accelerating voltage of 20 kV). UV−visible absorption spectra were recorded on a UV-visible spectrophotometer (JASCO V-550).

Photocurrent measurments were performed in a three-electrode setup with Pt counter electrode (2 cm × 3 cm) and SCE reference electrode. The electrolyte was purged with Ar for 30 min before photocurrent measurement and bubbled with Ar during the measurement. The light source was an

AM 1.5G sunlight similator (100 mW cm^{-2}) unless otherwise stated. Measurements of STH efficiency were carried out in a two-electrode system under AM 1.5G (100 mW cm^{-2}) light illumination and STH vales were caculated according to equation (1):

$$STH=\frac{\eta_F \times J_{\mathrm{sc}}\,(mA)\times 1.23V}{100\ mW\cdot cm^{-2}\times(A\mathrm{rea}_{BiVO_4}(cm^2)+A\mathrm{rea}_{Si}(cm^2))}\times 100\% \tag{1}$$

Measurements of gas evolutions were carried out in a two-electrode cell connected to a closed gas circulation and evacuation system as reported.[2] Typically, FeOOH/Mo:$BiVO_4$ (1 cm^2) or CoPi working electrode and p-Si NW or Si-cell counter electrode (0.5 cm^2) with a distance of 2 cm were immerged in 85 mL electrolyte. The system was thoroughly degassed and then irradiated by a 300 W Xe lamp in different modes. For CoPi vs. Si-cell, the light was illuminated from the Si-cell side. The electrochemical cell was maintained at 15 ± 2 ℃ by a cooling water bath during the reaction. Evolved O_2 and H_2 were analyzed by an online gas chromatograph with thermal conductivity detector (Agilent GC 7890, 5A zeolite column and Ar carrier).

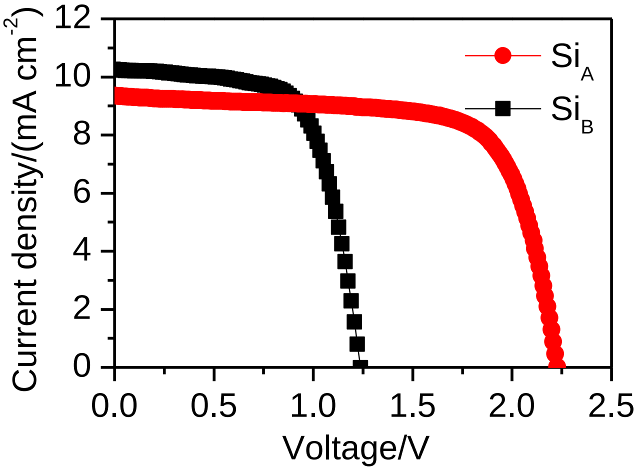

Fig. S1 I-V curves of Si solar cell (1 cm^2) under AM 1.5G sunlight (100 mW cm^{-2}) illumination

From Fig. S1, V_{oc} of Si_A and Si_B are 2.23 V and 1.22 V, respectively, and J_{sc} are 9.4 mA and 10.3 mA, respectively.

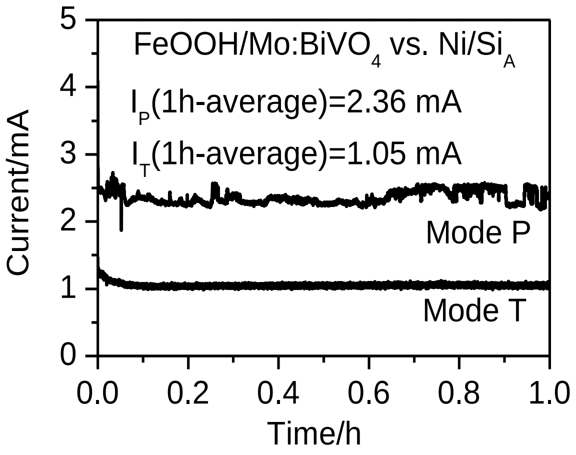

Fig. S2 Short-circuit I-t curves of the two-electrode system FeOOH/Mo:BiVO$_4$ photoanode vs. Si_A in Modes P and T. Light source: AM 1.5G sunlight simulator (100 mW cm^{-2}); Electrolyte: 0.5 M sodium phosphate (pH 7); Electrode areas: FeOOH/Mo:BiVO$_4$ 1 cm^2 and Ni/Si_A 1 cm^2.

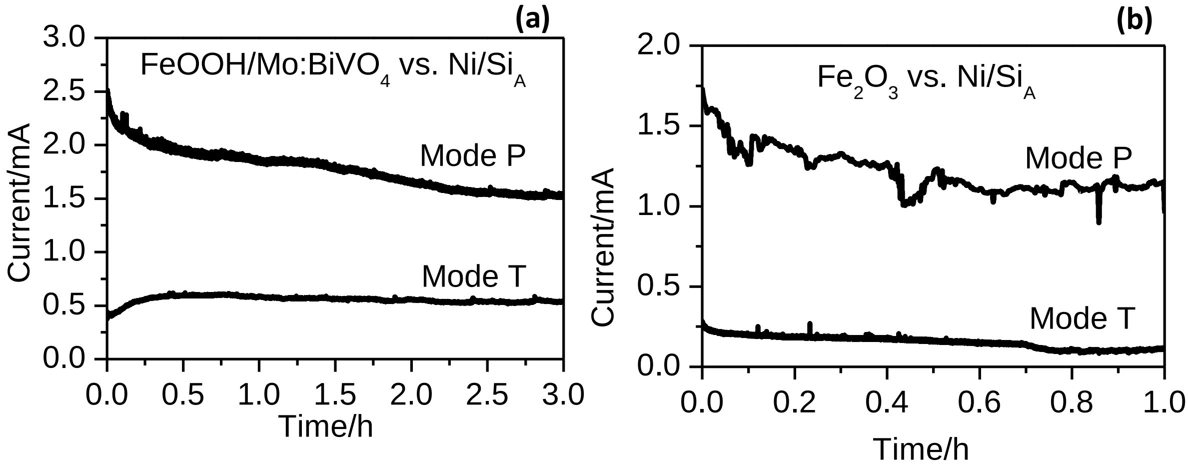

Fig. S3 Short-circuit I-t curves of the two-electrode system FeOOH/Mo:$BiVO_4$ and Fe_2O_3 photoanodes vs. Si_A in Modes P and T. Light source: AM 1.5G sunlight simulator (100 mW cm^{-2}); Electrolyte: 0.5 M sodium phosphate (pH 7); Electrode areas: FeOOH/Mo:$BiVO_4$ or Fe_2O_3 1 cm^2 and Ni/Si_A 0.5 cm^2.

Table S1 Analysis of the photovoltage loss of the coupled system Si_A vs. WO_3 photoanode in Modes P and T. V_{oc} is the open voltage of the coupled system, $V_{oc\text{-}Si}$ is the open voltage of Si1-cell itself, and V_{loss} is the photovoltage loss of the coupled system ($V_{loss} = V_{oc\text{-}Si} - V_{oc}$).

	Mode P			Mode T		
	$V_{oc\text{-}P}$/V	$V_{oc\text{-}Si\text{-}P}$/V	$V_{loss\text{-}P}$/V	$V_{oc\text{-}T}$/V	$V_{oc\text{-}Si\text{-}T}$/V	$V_{loss\text{-}T}$/V
Si_A vs.WO_3	1.7	2.23	0.53	1.6	2.17	0.57

From Table S1, for the coupled system Si_A vs. WO_3, the V_{loss} in Mode P is smaller than that in Mode T by 40 mV.

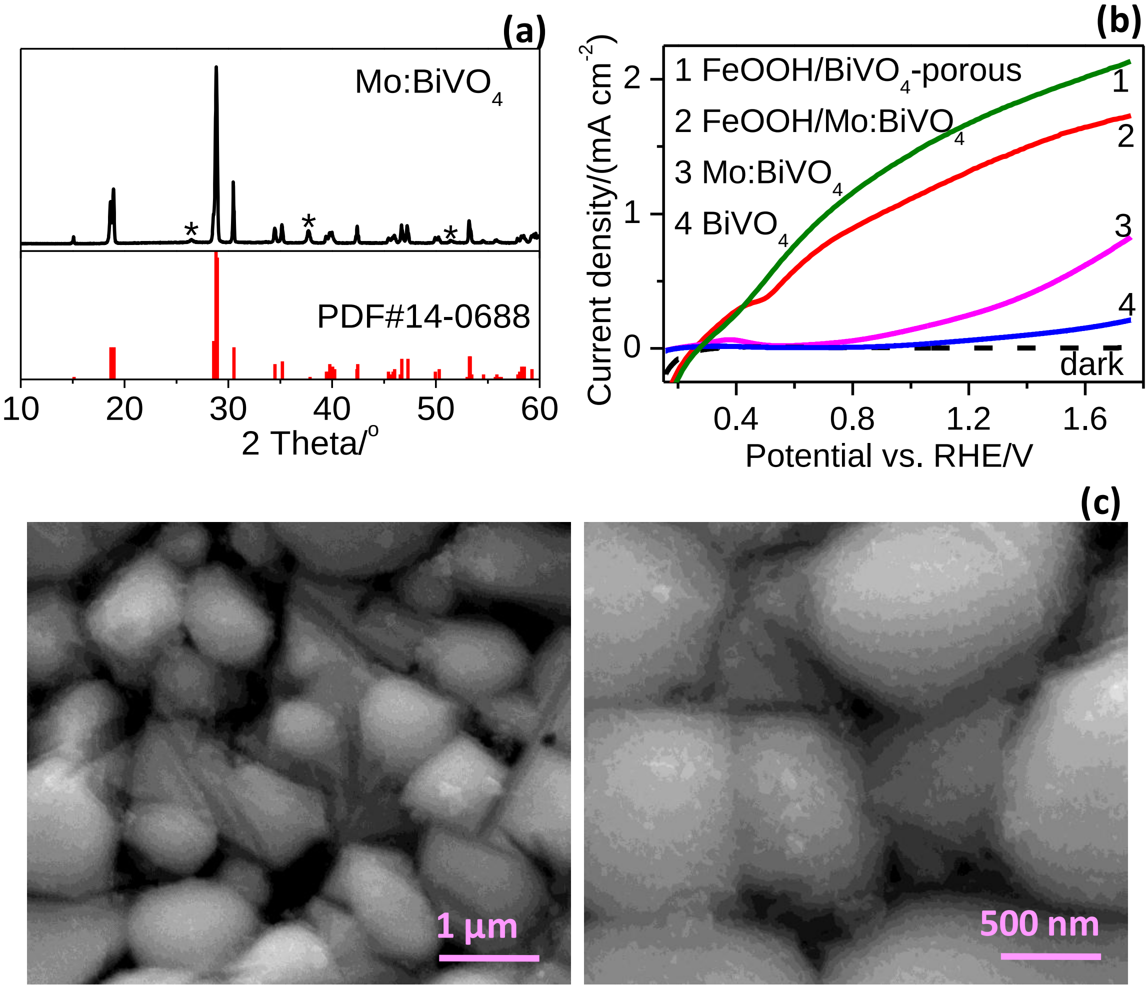

Fig. S4 (a) The XRD pattern of Mo:$BiVO_4$ electrode on FTO substrate (the peaks noted by * are FTO signals) and the standard monoclinic $BiVO_4$ XRD pattern (PDF# 14-0688); (b) Linear sweep voltammetric (LSV) scans of $BiVO_4$, Mo:$BiVO_4$, FeOOH/Mo:$BiVO_4$ and FeOOH/$BiVO_4$-porous photoanodes. Light source: AM 1.5G sunlight simulator (100 mW cm^{-2}); Scanning rate: 20 mV s^{-1}; Electrolyte: 0.5 M sodium phosphate (pH 7); (c) SEM images of FeOOH/Mo:$BiVO_4$ electrode;

Fig. S4 shows that Mo:$BiVO_4$ electrode is monoclinic phase. The photocurrent of Mo:$BiVO_4$ electrode is about twice of that of pristine $BiVO_4$ electrode. The photocurrent of Mo:$BiVO_4$ electrode is obviously increased and the onset potential is negatively shifted after loading a thin layer of FeOOH cocatalyst (Fig. S4 b, c), which is favorable for the dual-photoelectrode system.

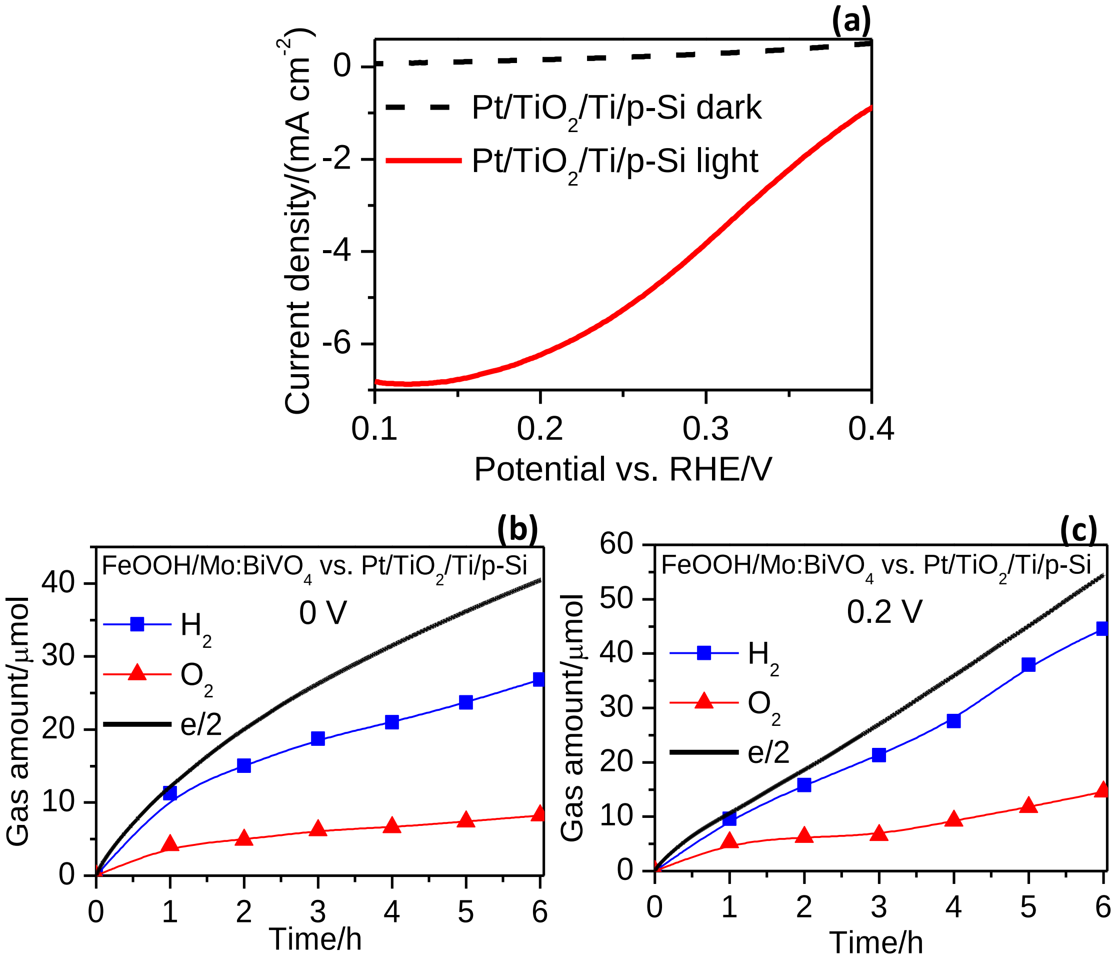

Fig. S5 (a) LSV scans of Pt/TiO$_2$/Ti/p-Si photocathode under AM 1.5G illumination (100 mW cm^{-2}) with a scanning rate of 20 mV s^{-1}, and (b, c) time courses of gas evolutions and corresponding e/2 amounts (solid lines) of the system FeOOH/Mo:BiVO$_4$ photoanode vs. Pt/TiO$_2$/Ti/p-Si with a bias of 0 V and 0.2 V under 300 W Xe lamp irradiation. Electrolyte: 0.5 M sodium phosphate (pH 7); Electrode areas: FeOOH/Mo:BiVO$_4$ 1 cm^2 and Pt/TiO$_2$/Ti/p-Si photocathode 1 cm^2.

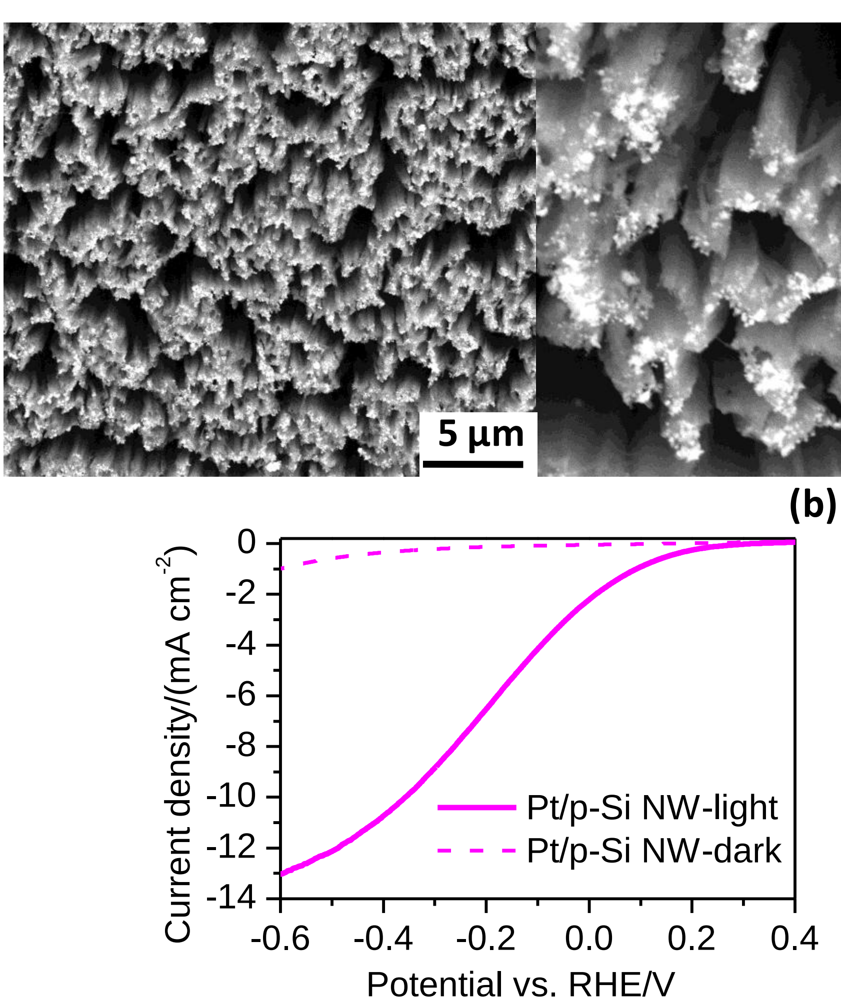

Fig. S6 (a) SEM images of Pt/p-Si electrode and (b) LSV scans of the Pt/p-Si photocathode. Light source: AM 1.5G sunlight simulator (100 mW cm^{-2}); Scanning rate: 20 mV s^{-1}; Electrolyte: 0.5 M sodium phosphate (pH 7).

Fig. S6 shows that the Pt/p-Si electrode shows nanowire array (NW) structure and plenty of Pt nanoparticles are decorated on tops of the nanowires. The as-prepared Pt/p-Si NW photocathode shows high cathodic photocurrent.

References

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